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1 **Co-adsorption and interaction mechanism of cadmium and**
2 **sulfamethazine onto activated carbon surface**

3
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16
17 **ABSTRACT**

18 Owing to their diverse functional groups, antibiotics can easily form complexes with heavy metals; the
19 complexation alters the migration and transformation behavior of both antibiotics and heavy metals. In this
20 study, we investigated the co-adsorption mechanism of sulfamethazine (SMT) and cadmium (Cd²⁺) heavy
21 metal ions and created an ideal water model containing two major contaminants: sulfamethazine and heavy
22 metal cadmium ions. Combined with the experimental analysis of the interaction mechanism, the results

23 indicate the heterogeneous multilayer adsorption of SMT on the surface of activated carbon (AC). The
24 bridging role of cadmium ions promotes the adsorption of SMT through the formation of SMT-Cd²⁺-AC
25 ternary complexes on the surface of activated carbon. Characterization experiments provided further insight
26 into the adsorption behavior of Cd²⁺ and SMT on activated carbon, revealing a strong correlation between
27 the Cd²⁺-SMT complexation and the SMT adsorption capacity. These results indicate that the effects of the
28 coexistence of antibiotics and heavy metal ions should be fully taken into account when investigating the
29 environmental behavior of antibiotics and heavy metal ions.

30

31 **Key words:** Heavy Metal, Antibiotics, Bridging, Complexation, Adsorption

32

33 **1. Introduction**

34

35 Fast industrialization and growing social activities result in the composition of wastewater becoming
36 increasingly more complex[1]. The combined pollution by antibiotics and heavy metals, widely affecting
37 actual water systems, is causing widespread concern[2, 3]. These two pollutants can cause serious harm to
38 humans and ecosystems[4]. The use of antibacterial agents in the livestock and poultry breeding industry,
39 the land use of livestock and poultry manure, and the centralized treatment of industrial wastewater have led
40 to increasingly serious pollution in surface water or groundwater[5]. Sulfanilamide antibiotics and cadmium
41 heavy metals are the most typical co-pollutants in livestock and poultry breeding industries[6, 7]. Cadmium
42 mainly originates from excessive use of Cd-containing chemicals (insecticides and fungicides) as well as
43 cadmium-rich feces[8]. Cadmium fertilizers are employed in domestic poultry breeding[9]. Synthetic
44 antibiotics have been used in livestock feed to improve feed efficiency and promote growth[10]. However,

45 foreign antibiotics are usually difficult to be absorbed by animals, and are directly discharged into the
46 receiving waters, where they may pose a serious threat to organisms and trigger antibiotic resistance[10].
47 Therefore, the efficient removal of antibiotics has attracted worldwide attention[11]. More importantly,
48 antibiotics can form complexes with coexisting metal ions[11-13], which may significantly alter their
49 chemical properties, migration/transformation process, and ecotoxic reactions[14]. For instance, it has been
50 reported that chelation with antacids (magnesium or aluminum salts) will change the bioavailability of
51 quinolones. Therefore, in environments co-polluted with heavy metal ions, complexation may have
52 unexpected environmental consequences[15].

53 Adsorption methods are the key approaches to study the transfer and transformation of pollutants in
54 the environment. Compared with coagulation, filtration, advanced oxidation, and other methods, the flexible
55 design/operation and low energy consumption of adsorption processes make them the preferred approach for
56 the practical production of clean water from wastewater, with high removal efficiency and less toxic
57 by-products. In addition, this green technology produces no sludge and is compatible with other water
58 treatment systems[16, 17]. Many groups are currently investigating the treatment of antibiotics and heavy
59 metals using adsorption methods. It has been reported that graphene oxide and ordered mesoporous carbon
60 materials with high adsorption capacity can effectively remove ciprofloxacin (CIP) pollutants in water[18,
61 19]. Li et al.[20] prepared a biochar sample that was used to remove tetracycline and sulfadiazine. In
62 addition, many detailed studies have focused on the removal of Cu^{2+} , Pb^{2+} [21], Hg^{2+} [22], Cr(VI) [23], and
63 Cd^{2+} [24] from water using carbon-based materials.

64 The combination of antibiotics and heavy metals has become a new component of polluted water.
65 Present research on the adsorption of single heavy metals or antibiotics does not reflect the current state of
66 environmental pollution. Relevant studies have shown that the presence of heavy metals can promote or

67 inhibit the adsorption process of different antibiotics, depending on the type and concentration of heavy
68 metals[25]. Na[26] and co-workers focused on two antibiotics commonly used in aqueous environments
69 (tetracycline hydrochloride and sulfadiazine) and two typical heavy metals (copper and zinc). Their results
70 showed that when antibiotics coexist with heavy metals in water, they can form complexes through
71 complexation. The cations of multivalent heavy metals can significantly enhance the adsorption of
72 antibiotics through the bridging effect[27–29]. For example, Cu(II) can improve the adsorption capacity.
73 The formation of CIP-Cu(II) complexes at pH values above 6.0 was simulated by surface complexation on
74 goethite[27]. The presence of Ni(II) promoted the adsorption of CIP on activated carbon (AC)[29]. The
75 mechanism by which metal ion complexation affects antibiotic adsorption is extremely complex. Although
76 some reports on the co-adsorption behavior of composite antibiotics and metal pollutants are available,
77 studies on the influence of metal ions on the adsorption of antibiotics are still scarce. In particular, the
78 mechanism of co-adsorption has not been investigated in sufficient detail. However, our understanding of the
79 mechanism controlling the influence of metal ions on the adsorption of antibiotics is still limited. At present,
80 the main metal ions involved in these studies are K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} , Ni^{2+} , and Fe^{3+} , whereas only few
81 investigations have focused on toxic heavy metal ions such as Cr^{6+} and Cd^{2+} [30]. The microscopic
82 characterization of the interaction between metal ions and antibiotics and of the mechanism by which metal
83 ion complexation affects antibiotic adsorption is still insufficient. Activated carbon has advantages such as
84 stable chemical properties, strong adsorption capacity, low cost, and wide availability. Therefore, the study
85 of the interfacial adsorption behavior of multiple pollutants on activated carbon will support the design of
86 cost-effective adsorbents[31, 32]. For this purpose, it is necessary to explore the co-adsorption and
87 interaction mechanism of antibiotics and heavy metals on the surface of activated carbon.

88 The aim of this study is to investigate the adsorption of antibiotics (sulfamethazine, SMT) and heavy

89 metals (cadmium) in single and binary contaminated solutions, and created an ideal water model containing
90 two major contaminants: sulfamethazine and heavy metal cadmium ions. The influence of other ions in the
91 natural environment was ignored temporarily. To more clearly observe the influence of cadmium ion on the
92 adsorption capacity of SMT and the influence of complexation on the adsorption, and to observe the changes
93 on the surface and inside of the adsorbent after adsorption in a short time, a relatively large concentration
94 range of SMT and Cd^{2+} was adopted in this study. First, we studied the adsorption behaviors of
95 sulfamethazine and cadmium ions on activated carbon in single and binary systems, based on the analysis of
96 adsorption kinetics and isotherms. Then, X-ray photoelectron spectroscopy (XPS), Raman, nuclear magnetic
97 resonance, and Fourier transform infrared (FTIR) spectroscopy techniques were used to characterize
98 adsorption changes in the binary system and the correlation between the complexation and the adsorption
99 amount. The analysis of the characterization and adsorption mechanism results allowed elucidating the
100 influence of complexation on the adsorption process, providing a comprehensive description of the
101 adsorption and interaction mechanism in the binary system.

102

103 **2. Materials and methods**

104

105 2.1 Materials

106

107 SMT antibiotic, cadmium chloride, and activated carbon were purchased from Sigma (St. Louis,
108 Missouri, USA), Tianjin Kemeo Chemical Reagent Co., Ltd., and Taishan Chemical Plant Co., Ltd.,
109 respectively. All reagents used in this study were of analytical grade and used without further purification.
110 Deionized water was used in the experiments.

111

112 2.2 Single system adsorption experiments

113

114 After determining the appropriate adsorption equilibrium time and amount of activated carbon, we
115 studied the effects of these parameters on the adsorption. In the experiment, 20 mg activated carbon was
116 used in a 150 mL test solution with a constant initial SMT concentration ($25 \text{ mg}\cdot\text{L}^{-1}$) and sufficient contact
117 time (24 h) at 303 K. A conical flask (250 mL, glass) was shaken with a water bath thermostatic oscillator at
118 200 rpm. Samples were collected at different time intervals, and an UV-Vis spectrophotometer was used to
119 scan the whole UV region and determine the adsorption equilibrium time of SMT. The dosage of activated
120 carbon was set to 5, 10, 20, 30, and 40 mg in a 150 mL test solution with constant initial antibiotic
121 concentration ($25 \text{ mg}\cdot\text{L}^{-1}$) and adsorption equilibrium time (12 h), in order to determine the optimal dosage
122 of adsorbent. In the experiment, 20 mg activated carbon was used in a 150 mL test solution with a constant
123 initial Cd^{2+} concentration ($25 \text{ mg}\cdot\text{L}^{-1}$) and sufficient contact time (24 h) at 303 K. A conical flask (250 mL,
124 glass) was shaken with a water bath thermostatic oscillator at 200 rpm. Samples were collected at different
125 time intervals, and inductively coupled plasma-atomic emission spectrometry(ICP-AES) was used to
126 determine the adsorption equilibrium time of Cd^{2+} . We investigated the adsorption behavior of SMT and
127 Cd^{2+} at different temperatures and carried out adsorption isotherm measurements. The temperature was set to
128 303, 313, and 323 K, and the water bath was shaken at 200 rpm under the above optimal conditions. We
129 determined the correlation between the equilibrium concentration and the adsorption capacity of SMT and
130 Cd^{2+} at different temperatures.

131

132 2.3 Binary system adsorption experiments

133

134 To explore the influence of cadmium on the adsorption of SMT, different Cd^{2+} concentrations (0, 25,
135 35, 45, 55, 65, 75, 100, 150, 350, 500, and 650 $\text{mg}\cdot\text{L}^{-1}$) were added to a 50 $\text{mg}\cdot\text{L}^{-1}$ SMT solution; then, 20
136 mg activated carbon was added and the water bath was shaken at a constant temperature (303K). To further
137 explore the adsorption behavior of SMT and cadmium ions in a binary system, we selected a concentration
138 ratio of 1:1 between antibiotic and cadmium ions. The adsorption isotherm experiments were carried out at
139 three different temperatures (303, 313, 323K).

140

141 2.4 Characterization and analysis of AC- Cd^{2+} -SMT ternary complex

142

143 FTIR spectra were obtained on a vertex 70 spectrometer (Thermo Fisher, USA) to analyze the changes
144 of surface functional groups before and after adsorption of activated carbon. The functional groups and
145 binding energy of elements at the surface of AC were analyzed by X-ray photoelectron spectroscopy (XPS,
146 Thermo Fisher ESCALAB 250Xi, United States), which was carried out on a Kratos Axis Ultra DLD
147 spectrometer using monochromated Al $\text{K}\alpha$ X-rays at a power of 150 W. All XPS test samples were
148 freeze-dried in advance. Raman spectra were obtained by Renishaw (Hoffman Estates) equipped with
149 argon-ion laser to analyze the change of graphitization degree of activated carbon before and after the
150 adsorption. Nuclear magnetic resonance (NMR) spectroscopy (Bruker Avance 400) was used to determine
151 the chemical shifts of surface elements of SMT before and after adding Cd^{2+} .

152

153 2.5 Determination of sulfamethazine and cadmium ions

154

155 The concentration of sulfamethazine was determined by a UV-Vis spectrophotometer; the absorbance
156 was measured using deionized water as blank control, at a SMT maximum absorption wavelength of 261 nm.
157 The concentration of cadmium ions was determined by inductively coupled plasma-atomic emission
158 spectrometry (ICP-AES).

159

160 2.6 Data analysis

161

162 The adsorption capacity of sulfamethazine and cadmium ions [q_e ($\text{mg}\cdot\text{g}^{-1}$)] was calculated by equation

163 (1) [33]:

164

$$165 \quad q_e = (C_0 - C_e) \cdot V/M \quad (1)$$

166

167 where C_0 and C_e ($\text{mg}\cdot\text{L}^{-1}$) are the initial and equilibrium concentrations of SMT or Cd^{2+} before and after
168 adsorption, respectively, while V (mL) and M (mg) are the added volume of SMT or cadmium ion solutions
169 and the mass of activated carbon, respectively.

170 The linearized Langmuir model (Eq. (2)) and Freundlich model (Eq. (3)) were performed for the
171 adsorption isotherms of SMT and Cd^{2+} to evaluate the distribution of SMT and Cd^{2+} in the solid phase and
172 liquid phase after achieving adsorption equilibrium[34]:

173

$$174 \quad C_e/q_e = C_e/q_{max} + 1/(K_L \hat{A} \cdot q_{max}) \quad (2)$$

175

$$176 \quad \ln q_e = \ln K_F + 1/n \cdot \ln C_e \quad (3)$$

177

178 where q_{\max} ($\text{mg}\cdot\text{g}^{-1}$) is the maximum adsorption concentration of SMT and Cd^{2+} per unit mass of AC.

179 $K_L(\text{L}\cdot\text{mg}^{-1})$ and $K_F(\text{L}\cdot\text{mg}^{-1})$ are respectively the adsorption constant of Langmuir and Freundlich models.

180 $1/n$ are the adsorption intensity constant of Freundlich. $C_0(\text{mg}\cdot\text{L}^{-1})$ is the initial concentration of SMT, and

181 the complexation ratio of SMT to Cd^{2+} is 1:1[35]. The relationship between the concentration of SMT and its

182 adsorption capacity is known; the concentration of the complex can be calculated based on the concentration

183 of SMT and the complexation ratio[35], and the correlation between the complex concentration and the

184 SMT adsorption capacity can thus be determined[36, 37].

185

186 **3. Results and discussion**

187

188 3.1 Single adsorption of SMT and Cd(II) on activated carbon

189

190 As shown in Fig. 1a, the adsorption equilibrium time of SMT on activated carbon was approximately

191 12 h. The adsorption of SMT on AC showed no significant differences at pH 3–7. At pH 9, the effect of SMT

192 adsorption on AC was weaker than that observed under acidic and neutral conditions. As a typical

193 amphoteric compound, SMT presents different proton states (SMT^+ , SMT^- , and SMT) at different pH

194 values[38]. When the initial pH value of the solution was 3–7, the adsorption of SMT by AC was significant.

195 This is because, at pH 3–5, SMT mainly exists as a protonated neutral molecule. At pH 5, the removal rate of

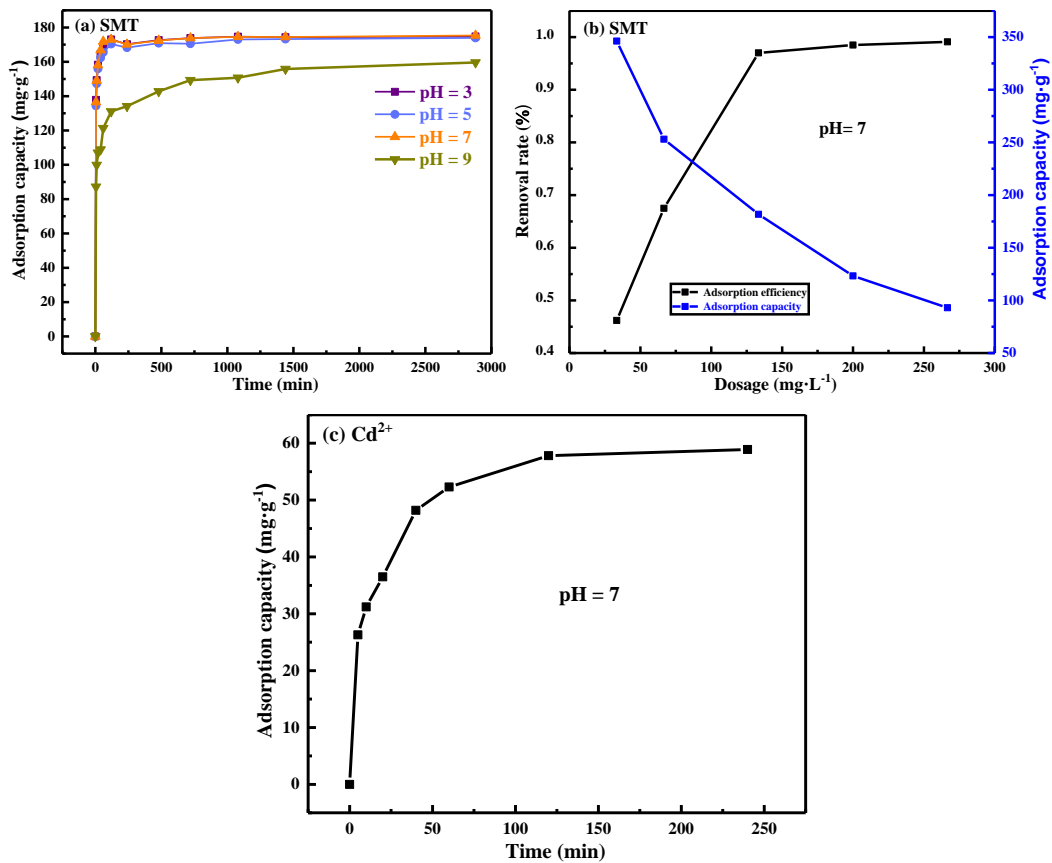
196 SMT reached 93.9%, indicating a high neutral adsorption capacity. After that, with increasing pH, the SMT^-

197 anion becomes the main species in the solution, the electrostatic repulsion between SMT and AC increases,

198 so that the adsorption capacity of SMT also decreases [39].

199 The determination of the adsorption equilibrium time of cadmium ions on activated carbon is shown in
200 Fig. 1c. The Cd^{2+} adsorption equilibrium was reached at approximately 2 h. The results of this study are
201 generally consistent with previous reports (Figs. 1a and 1c)[[18](#), [19](#), [38](#)]. Meanwhile, this study focuses on
202 the effect of cadmium ions on the adsorption capacity of SMT, to accurately approach the typical pH value
203 of an actual water body containing SMT contaminant(pH=7), the single adsorption experiment of cadmium
204 ion and the subsequent experiments of this study were carried out under the condition of pH = 7[[40](#), [41](#)].

205 The effect of the AC dosage on the adsorption removal of SMT was further studied (Fig. 1b). With the
206 optimum AC dosage, the adsorption of SMT is expected to reach the maximum. The effect of the AC dosage
207 on the SMT adsorption was investigated by adding different amounts of AC to the solution. The results show
208 that the removal rate of SMT increased from 46.2% to 99.1% as the AC dosage increased from 33.33 to
209 $266.67 \text{ mg}\cdot\text{L}^{-1}$, due to the increased number of adsorption sites on the adsorbent surface. When the amount of
210 AC was further increased, the removal rate of SMT remained almost unchanged, due to the decrease in the
211 adsorption capacity per unit mass of adsorbent. At higher adsorbent concentrations, the effective surface area
212 decreases, and the aggregation or overlap between adsorption sites leads to a decrease in the available
213 adsorbent surface area and an increase in diffusion path length. Some of the examined adsorbent systems fail
214 to reach adsorption saturation, which is consistent with the results of previous studies[[26](#)]. Considering
215 adsorption effects, adsorption capacity, and economic factors, the optimal adsorbent dose was estimated to
216 be $133.33 \text{ mg}\cdot\text{L}^{-1}$.



217

218

219 **Fig. 1.** Effect of contact time (a) and adsorbent dosage (b) on adsorption of SMT; (c) effect of contact time on

220

adsorption of Cd(II).

221

222 3.2 Co-adsorption of SMT and Cd(II) on activated carbon

223

224 Compared with the single-contaminant system, the binary contaminant solution composed of

225 antibiotics and heavy metals showed a significantly different adsorption behavior. As shown in Fig. 2, at a

226 solution pH of 7, when the cadmium ion concentration increased from 0 to 650 mg·L⁻¹, the synergistic effect

227 of Cd²⁺ promoted the SMT adsorption on AC. Previous reports speculated that heavy metals acting as

228 electron acceptors have the ability to form Cd²⁺-SMT complexes by coordination and electrostatic adsorption,

229 providing more adsorption sites for SMT in water, thus promoting the adsorption process[33, 42].

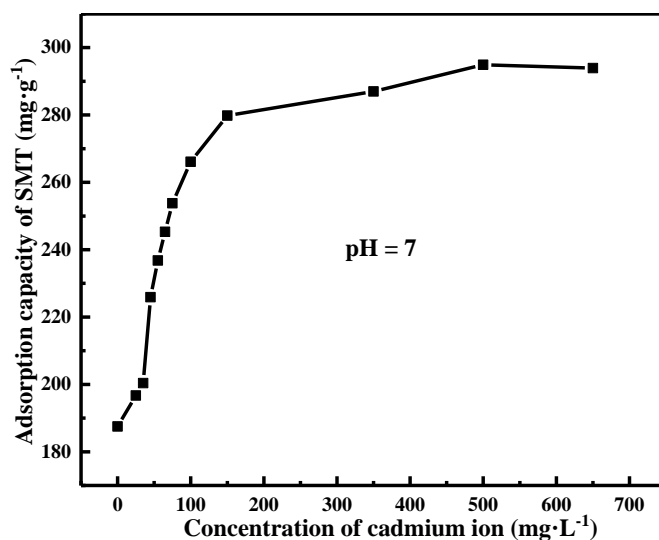


Fig. 2. Effect of cadmium ion concentration on adsorption of SMT.

230

231

232

233 Figs. 3a and 3b show the adsorption isotherms of SMT in the single and binary systems, respectively.

234 The Freundlich model was more suitable for SMT adsorption ($R^2=0.959/0.982/0.954$ for SMT with Cd^{2+} ,

235 and $0.61/0.145/0.485$ without Cd^{2+}) than the Langmuir model ($R^2=0.942/0.94/0.949$ for SMT with Cd^{2+} , and

236 $0.932/0.896/0.903$ without Cd^{2+}), which can be described as heterogeneous multilayer adsorption (Table 1).

237 Compared with the system without Cd^{2+} , the presence of Cd^{2+} increased the adsorption capacity of SMT on

238 activated carbon. In particular, the addition of Cd^{2+} significantly promoted the adsorption of SMT on

239 activated carbon, which is consistent with the results of Fig. 2a. Relevant studies have shown that organic

240 ligands bound with heavy metals can interact with functional groups on the surface of activated carbon to

241 form stable complexes[43]. Higher numbers of electron-rich groups such as N and O in antibiotics lead to a

242 stronger complexation ability with metal ions. Therefore, it can be further speculated that the organic ligands

243 bound to cadmium ions may undergo complexation reactions with the functional groups on the surface of

244 activated carbon, even though the numbers and types of different functional groups in sulfonamides are

245 limited, and the N-containing functional groups are mainly involved in the coordination[44]. The study has

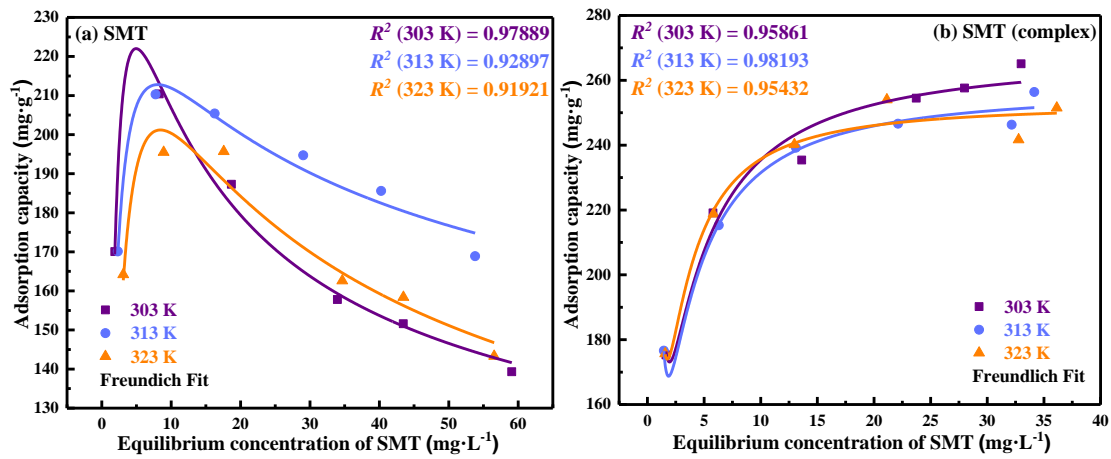
246 shown that bridging by metal centers is one of the most important mechanisms for the adsorption of

247 antibiotics on adsorbents[26]; this may explain how Cd²⁺ can promote the adsorption of SMT on activated
 248 carbon, which will be further confirmed by the experiments described in the following.

249 **Table 1** Calculated Langmuir and Freundlich parameters of SMT adsorption isotherms

Models	Parameters	SMT			SMT(complex)		
		303K	313K	323K	303K	313K	323K
Langmuir	$q_{\max}(\text{mg}\cdot\text{g}^{-1})$	216.3	215.4	201.9	266.304	257.462	253.772
	$K_L(\text{L}\cdot\text{mg}^{-1})$	3.191	9.062	2.383	1.131	1.479	1.375
	R^2	0.61	0.145	0.485	0.922	0.92	0.919
Freundlich	$K_F(\text{L}\cdot\text{mg}^{-1})$	8.329	9.069	9.235	8.732	7.219	6.251
	n	0.665	0.716	0.793	0.699	0.809	0.803
	R^2	0.979	0.929	0.919	0.959	0.982	0.954

250



251

252 **Fig. 3.** Adsorption isotherms of SMT in single (a) and binary (b) systems, along with Freundlich model fits.

253

254 Figs. 4a and 4b show the adsorption isotherms of Cd²⁺ in the single and binary system, respectively.

255 The adsorption amount of Cd²⁺ decreased after SMT was added to the system. This can be explained by

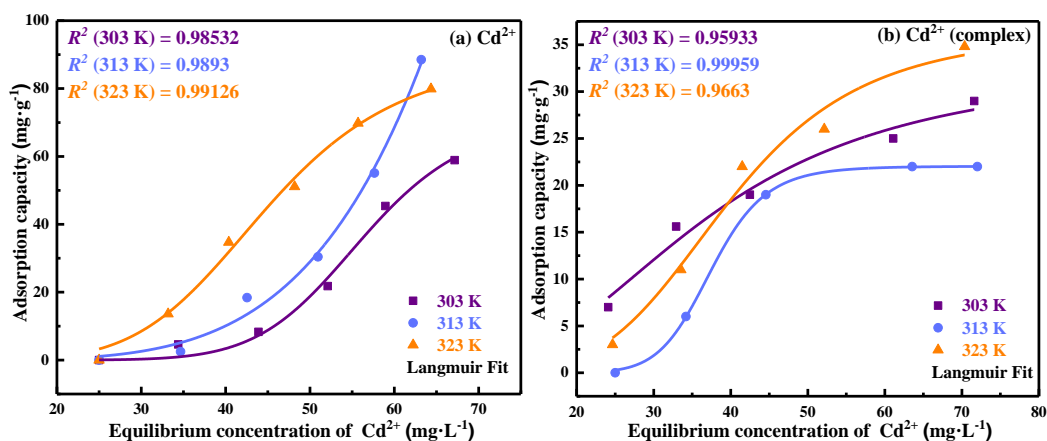
256 assuming that the adsorption of Cd²⁺ was inhibited by the complexation with SMT, which thus reduced the

257 adsorbed Cd^{2+} amount. The addition of cadmium ions initially promoted the adsorption of SMT; however,
 258 when the Cd^{2+} concentration was further increased, no further increase in SMT adsorption was observed.
 259 This suggests a monolayer adsorption behavior of cadmium ions on activated carbon, which cannot further
 260 promote the adsorption of SMT at higher Cd^{2+} concentrations[25]. The Langmuir model was more suitable
 261 for Cd^{2+} adsorption ($R^2=0.959/0.999/0.966$ for Cd^{2+} with SMT, and $0.985/0.989/0.991$ without SMT) than
 262 the Freundlich model ($R^2=0.932/0.926/0.903$ for Cd^{2+} with SMT, and $0.932/0.896/0.903$ without
 263 SMT)(Table 2). When the atomic sites on the surface of activated carbon are unsaturated, Cd^{2+} will be
 264 adsorbed on the surface. After the adsorption of one layer of Cd^{2+} ions, the original unsaturated sites become
 265 saturated, and no further adsorption on the activated carbon is possible. Due to the strong interaction
 266 between the functional groups on the surface of activated carbon and Cd^{2+} , the adsorption of the latter tends
 267 to be uniform, resulting in a single-layer covering. This is consistent with the Langmuir isotherm model of
 268 monolayer adsorption[45].

269

270 **Table 2** Calculated Langmuir and Freundlich parameters of Cd^{2+} adsorption isotherms

Models	Parameters	Cd^{2+}			Cd^{2+} (complex)		
		303K	313K	323K	303K	313K	323K
Langmuir	$q_{\max}(\text{mg}\cdot\text{g}^{-1})$	59.6	88.55	81.2	32.744	22.036	36.455
	$K_L(\text{L}\cdot\text{mg}^{-1})$	0.216	0.318	0.497	0.315	0.357	0.418
	R^2	0.985	0.989	0.991	0.959	0.999	0.966
Freundlich	$K_F(\text{L}\cdot\text{mg}^{-1})$	2.528	2.324	2.084	2.098	2.097	2.098
	n	0.464	0.421	0.452	0.451	0.453	0.469
	R^2	0.932	0.896	0.903	0.932	0.926	0.903



272

273 **Fig. 4.** Adsorption isotherms of Cd(II) in single (a) and binary (b) systems, along with Langmuir model fits.

274

275 3.3 Effect of complexation on co-adsorption

276

277 3.3.1 FTIR analysis of adsorption mechanism

278 FTIR spectroscopy was used to determine changes in the surface functional groups before and after

279 adsorption. And the FTIR spectra of Cd²⁺, SMT and SMT+Cd²⁺ adsorbed on activated carbon were280 compared (Fig. 5). In the a–d spectra(Fig.5), the peak at 3445 cm⁻¹ is the characteristic peak of -OH (from281 phenol or alcohol) and the tensile vibration of water adsorbed on AC [46, 47]. The peak at 1412cm⁻¹ is the

282 stretching vibration band of C-O-C, C=C, or C-H on the surface of activated carbon [47, 48], the

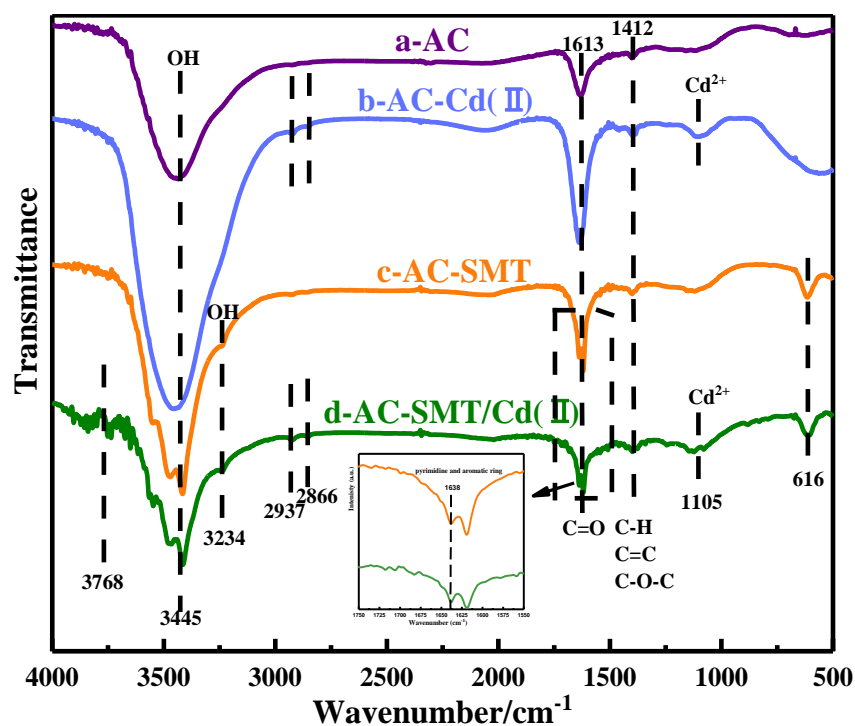
283 characteristic peak at 1613 cm⁻¹ may be attributed to the C=O tensile vibration on the AC surface [46, 47].284 The peak at 1638 cm⁻¹ indicated that the band has the characteristic of aromatic ring stretching mode. After

285 SMT was adsorbed on AC (c, d spectrum, Fig.5), there are one or more aromatic rings in the AC structure,

286 corresponding to the pyrimidine ring structure and aromatic ring in SMT [46]. And there is an obvious

287 characteristic peak at 3234 cm⁻¹, which may correspond to the stretching vibration of -OH [48]. In the b, d288 spectra (Fig. 5), the peak at about 1105 cm⁻¹ was significantly enhanced, which is a strong characteristic

289 peak for the adsorption of heavy metal Cd^{2+} [49]. Under neutral conditions, SMT mainly exists in the form
 290 of SMT^0 and SMT^- [50]. When Cd^{2+} was added, the H part on the Sulfonamide group is ionized to form a
 291 negatively charged SMT^- , which can be complexed with Cd^{2+} by replacing H^+ [51, 52]. Therefore, in the
 292 spectrum d (Fig. 5), the significant fluctuations at 3234cm^{-1} - 3445cm^{-1} indicated that it is the vibration and
 293 fracture of $-\text{NH}$ in SMT, which complexes with Cd^{2+} by substituting H at the N atom[53]. After Cd^{2+} was
 294 adsorbed on AC, new characteristic peaks appeared at 2937cm^{-1} and 2866cm^{-1} , and this change was still
 295 observed in AC-Cd^{2+} -SMT samples, indicating the formation of AC-Cd^{2+} -SMT ternary complex [49]. At the
 296 same time, the outermost shell of the Cd^{2+} nucleus had an empty orbital that can accommodate lone pair
 297 electrons, while oxygen, sulfur, nitrogen, and other atoms are typical lone pair electron donors [54]. It can be
 298 speculated that the N atoms in the pyrimidine ring participate in the complexation process. The analysis of
 299 the structure of the SMT molecule suggested that multiple interactions can be involved in the complexation
 300 process at the same time.



301

302 Fig. 5. FTIR spectra of (a) AC before adsorption, (b) Cd(II)-adsorbed AC, (c) SMT-adsorbed AC, and (d)

SMT/Cd(II)-adsorbed AC.

303

304

305 3.3.2 XPS analysis of adsorption mechanism

306 **Table 3**

307 Elemental composition of AC, SMT-adsorbed AC, Cd(II)-adsorbed AC, and SMT/Cd(II)-adsorbed AC

Name	Elemental analysis (atom based) (%)				
	C	O	N	S	Cd
AC	91.89	7.41	0.7	^a	^a
AC-SMT	85.89	8.79	4.29	1.03	^a
AC-Cd(II)	92.09	6.93	0.85	^a	0.13
AC-Cd(II)-SMT	84.38	7.7	5.81	1.97	0.15

308 ^a not detected.

309

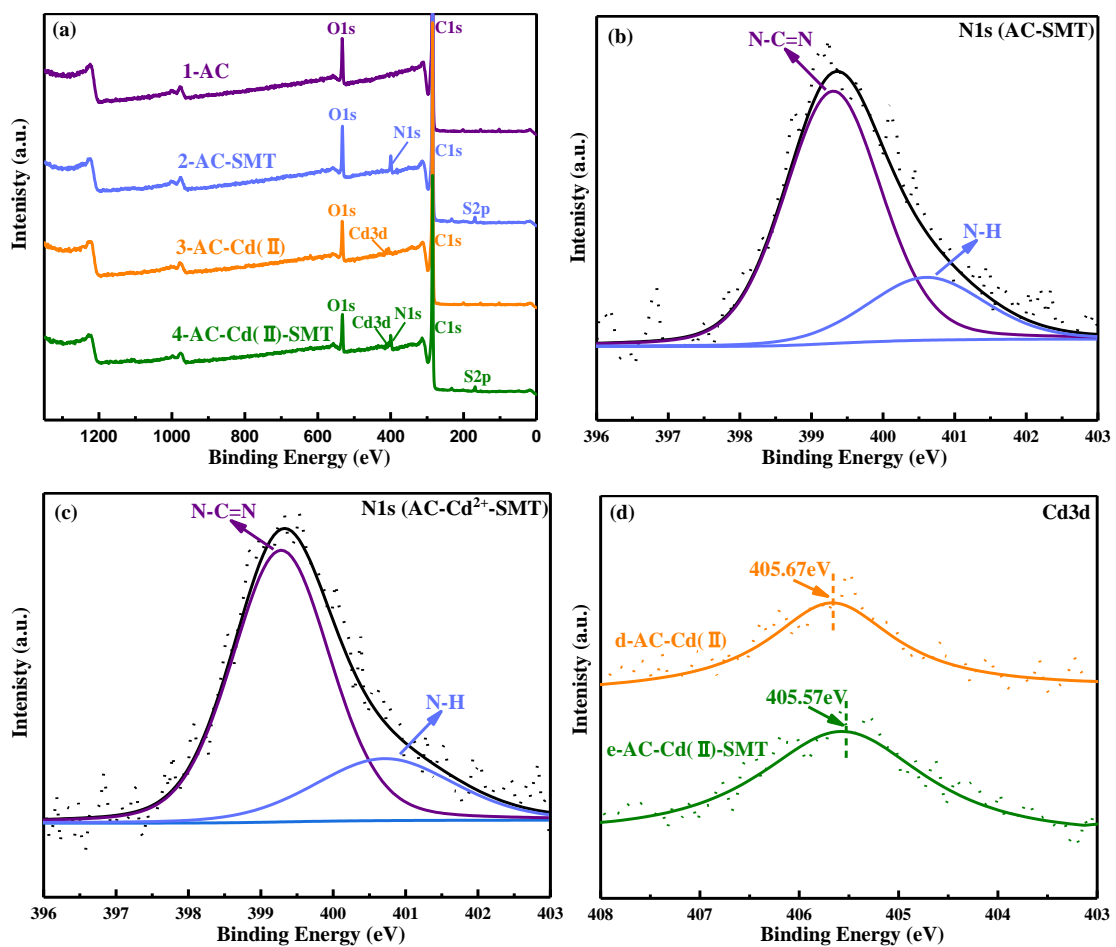
310 As shown in Fig. 6a, the XPS profile of the single AC sample shows typical C1s and O1s peaks at
311 284.8 and 532.6 eV. After adsorption of Cd(II), a Cd3d peak at 416.54 eV appears in the XPS profile, and
312 Table 1 shows a percentage of Cd(II) compared with the AC sample, indicating that Cd metal ions were
313 adsorbed on the adsorbent surface. The adsorption of Cd²⁺ mainly relied on the electrostatic attraction
314 between AC surface and Cd²⁺ due to deprotonation[33], which proves that there was some kind of binding
315 interaction between them. SMT co-adsorption led to the simultaneous appearance of N1s and S2p peaks, as
316 shown in Fig. 6a. Compared with the AC sample, the N content in the AC-SMT system was significantly
317 higher, confirming that SMT was adsorbed on the surface. The N content further increased in the ternary
318 system, which indicates that the presence of Cd²⁺ promotes the adsorption of SMT. Cadmium ions are first

319 adsorbed by cation- π interactions and then diffuse to other adsorption sites. Although the cation- π interaction
320 does not promote the adsorption of SMT, cadmium species adsorbed at other sites may form SMT-Cd²⁺-AC
321 complexes with negatively charged SMT, and Cd²⁺ ions at a certain concentration can enhance the
322 adsorption of SMT[55].

323 The N1s peak decomposes into two related peaks: N-C=N(399.3eV) and -NH(400.6eV)(Figs.5b and
324 5c) [56]. According to the peak area calculation of Fig.5b and Fig.5c, it can be concluded that the -NH part
325 of the system is reduced (the peak area is reduced from 1307.15 to 1198.3) with the addition of Cd²⁺.
326 Moreover, the binding energy of -NH shifted from 400.6eV to 400.71eV, while that of N-C=N shifted from
327 399.3eV to 399.24eV. It is revealed that -NH in SMT is the main functional group involved in complexation,
328 and N on the pyrimidine ring may also participate in complexation [49].

329 As shown in Fig. 6d, the binding energies of Cd(II) adsorbed in the binary system were shifted to
330 lower values, showing that the changes in chemical bonding after adsorption on AC in the binary system
331 resulted in a red shift of the XPS signals relative to those of the single heavy metal system. This means that
332 the metal ions are in their reduced state in the presence of SMT[33]; the electrons involved in the reduction
333 process are generated from the breaking of the N-H bond of SMT, which indicates that the metal cations
334 interact with the N atoms (acting as electron donors) to form a complex after the N-H bond cleavage (Figs.
335 5b and 5c). This is consistent with the previous FTIR spectroscopy results. The atomic percentages obtained
336 from the peak areas show that the metal ions enhanced the adsorption of SMT (from 4.29% to 5.81%; Table
337 3), which is consistent with the adsorption isotherm experiments obtained for the SMT-Cd²⁺ system (Fig.3b).
338 Therefore, at a certain concentration of Cd²⁺, the AC-Cd²⁺-SMT ternary complex is formed through metal
339 cation bridging. The cadmium ion acts as a bridge, indirectly connecting SMT with the adsorbent[57]. In the
340 absence of cadmium ions, the surface functional groups of SMT molecules and adsorbents are negatively

341 charged. The corresponding electrostatic repulsion impairs the adsorption performance of activated carbon.
 342 The presence of cadmium ions effectively reduces the electrostatic repulsion between SMT and activated
 343 carbon. The small hydration radius of cadmium ions results in a strong ability to form coordination
 344 complexes with SMT under neutral conditions. Hence, the bridging effect of Cd cations is relatively strong,
 345 which provides more adsorption sites for SMT in water; this can promote the adsorption of SMT, thus
 346 improving the efficiency of its removal process[58].



347

348

349 **Fig. 6.** (a) Full-scan XPS profiles of AC before adsorption (1), SMT-adsorbed AC (2), Cd(II)-adsorbed AC (3), and

350 SMT/Cd(II)-adsorbed AC (4). XPS N1s deconvolution peak resolution of (b) SMT-adsorbed AC; (c)

351 SMT/Cd(II)-adsorbed AC; (d) Cd3d binding energy change between single and binary systems.

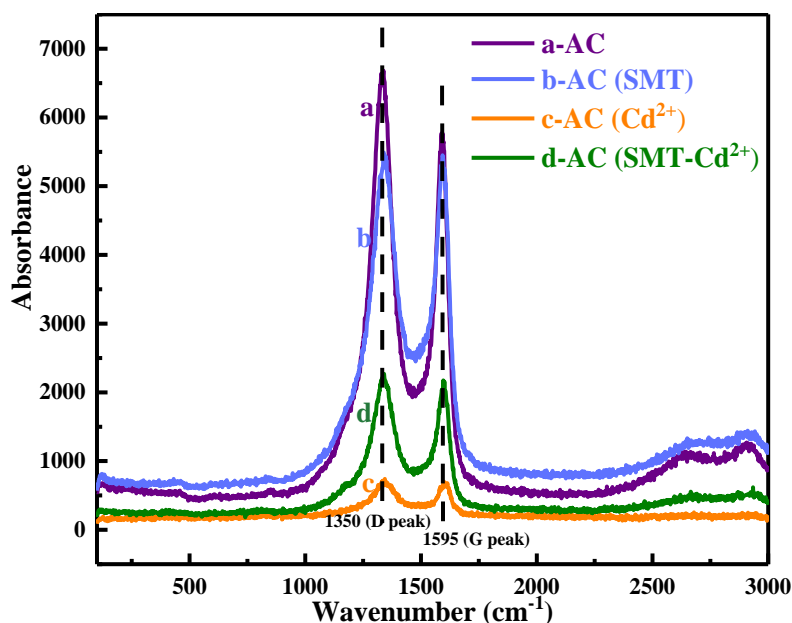
352

353 3.3.3 Raman and NMR analysis of adsorption mechanism

354 The Raman spectra of the four solids (Fig. 7) show two peaks. The first, near 1595 cm^{-1} (G peak, sp^2
355 C), is the characteristic scattering peak of graphite, whereas the second peak at 1350 cm^{-1} (D peak, sp^3 C) is
356 due to lattice defects, disorder, and low-symmetry sites in the carbon structure of graphite[59]. The Raman
357 intensities are related to the structural order of the carbon sheets. The ID/IG ratio (where ID and IG are the
358 intensities of the D and G peaks, respectively) is sensitive to the graphitization degree, which is the
359 parameter used to measure the defect density of activated carbon[60]. Therefore, the graphitization degree of
360 a carbon material can be evaluated using the $R = \text{ID}/\text{IG}$ parameter. A smaller R value corresponds to a higher
361 degree of graphitization[61]. The ID and IG values are obtained by calculating the peak areas of peak D and
362 peak G, and the relative intensity ratio of ID/IG is obtained[62]. The R values of the four Raman spectra
363 were 2.06 (AC), 2.20 (AC- Cd^{2+}), 1.98 (AC-SMT), and 1.936 (AC-SMT/ Cd^{2+}). The D band at 1350 cm^{-1} is a
364 defect-induced feature, which reflects the imperfect crystal structure of carbon. Compared with AC, the
365 ID/IG value of the AC- Cd^{2+} system increased from 2.06 to 2.2, which indicates that more structural defects
366 were formed on Cd^{2+} -doped AC[63], resulting in a more disordered AC structure. However, the ID/IG
367 values of SMT and SMT/ Cd^{2+} decreased from 2.06 to 1.98 and 1.936, respectively, indicating a reduced
368 defect density and higher graphitization degree of carbon. This type of activated carbon substrate will
369 provide more binding sites for the adsorption process; in other words, the high degree of graphitization can
370 promote the adsorption process[64], thus enhancing the adsorption of SMT, up to a certain extent[48]. In
371 agreement with the above FTIR analysis, with the enhanced SMT adsorption, the formation of the Cd^{2+} -SMT
372 complex on the activated carbon surface promoted the adsorption of SMT.

373 As the hydrogen atoms of amino groups on the benzene ring are highly active, they are likely to be
374 replaced by deuterium in a deuterated solution[36, 65, 66]; hence, it is difficult to observe the corresponding
375 peak in the NMR spectra in Fig. 8. The first peak, which is located at high fields (2–3 ppm) and exhibits a

376 large integral, corresponds to the four hydrogen atoms in the benzene ring. The second signal is a single peak
377 at 5 ppm, corresponding to the hydrogen of the -NH- group connected to the pyrimidine ring; the third peak,
378 with a chemical shift of 6–8 ppm, corresponds to three hydrogen atoms on the pyrimidine ring. The presence
379 of cadmium ions results in an obvious decrease in the intensity of the four-hydrogen peak on the benzene
380 ring, and the corresponding signal partially disappears; moreover, the signal of the hydrogen atom in the
381 -NH- group connected to the pyrimidine ring also disappears. This behavior could be attributed to the
382 breaking of the N-H bond and the complexation of Cd(II). In addition, the third peak at 6–8 ppm,
383 corresponding to the hydrogen atoms in the pyrimidine ring, almost disappears. It can be concluded that,
384 after adding Cd²⁺, part of the hydrogen atoms on the pyrimidine ring will be ionized, and their corresponding
385 signal will thus disappear.



386
387 **Fig. 7.** Raman spectra of (a) AC before adsorption, (b) SMT-adsorbed AC, (c) Cd(II)-adsorbed AC, and (d)
388 SMT/Cd(II)-adsorbed AC.
389

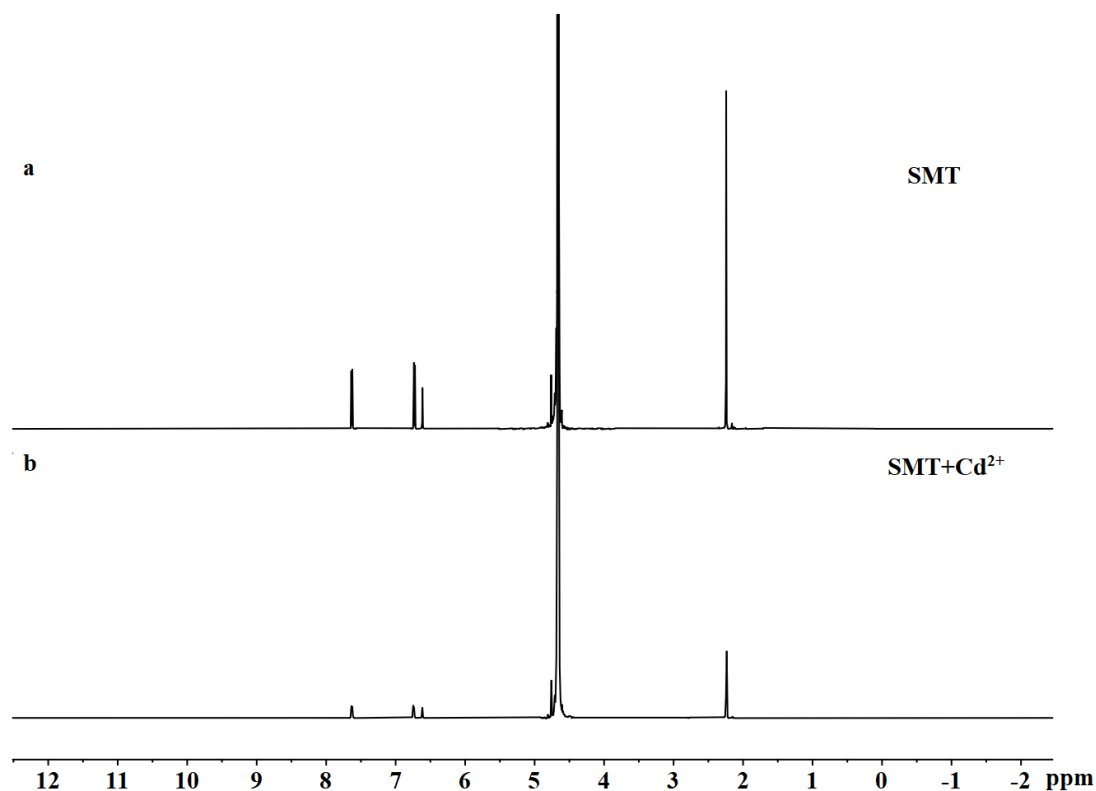


Fig. 8. ¹H NMR spectra of (a) SMT and (b) SMT-Cd(II).

3.3.4 Correlation between SMT-Cd(II) complexation and adsorption capacity

To further understand the influence of the complexation of Cd²⁺ and SMT on the adsorption properties of activated carbon, the adsorption capacity was plotted vs. the calculated concentration of the complex, to determine the possible relationship between the complexation of Cd²⁺ and SMT and their mutual adsorption.

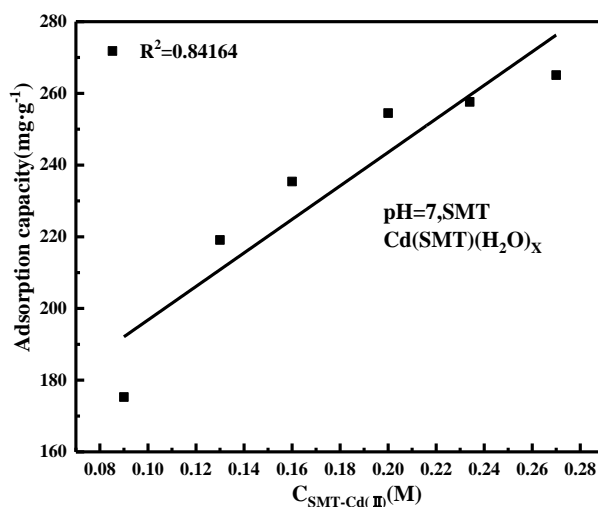
The correlation between the concentration of SMT and its adsorption capacity had been studied in a previous paper, which confirmed that SMT forms a complex with Cd²⁺ in a 1:1 ratio (SMT and Cd²⁺ react in a 1:1 ratio)[67-69]. Therefore, the concentration of the complex can be calculated from the SMT concentration

and the complexation ratio. The relationship between the concentration of the complex and the adsorption capacity of SMT was plotted in Fig. 9, a linear regression analysis was performed, which highlights a good

correlation between the concentration of Cd²⁺-SMT and the SMT adsorption amount ($R^2 = 0.84164$)[37].

These results show that the complexation of Cd²⁺ and SMT has a significant effect on the adsorption of SMT

404 under neutral conditions.



405

406

Fig. 9. Correlation between complexation ratio and adsorption capacity.

407

408 3.3.5 Co-adsorption mechanism of SMT and Cd(II)

409 As shown in Fig. 10, SMT is adsorbed *via* a heterogeneous multilayer process, involving water and

410 p-p stacking interactions between porous activated carbon and SMT[70]. It is well known that p-p stacking

411 interactions can explain the adsorption mechanism of aromatic substances on a layered activated carbon

412 surface. Therefore, the molecular structure of SMT enables p-p stacking interactions between the benzene

413 ring (p-electron acceptor) and the p-rich activated carbon adsorbent[50]. As an amphoteric molecule, SMT

414 contains different charged or electron-rich groups. Therefore, electrostatic interactions may be established

415 between the various functional groups of SMT and the corresponding surface structure of porous activated

416 carbon[71].

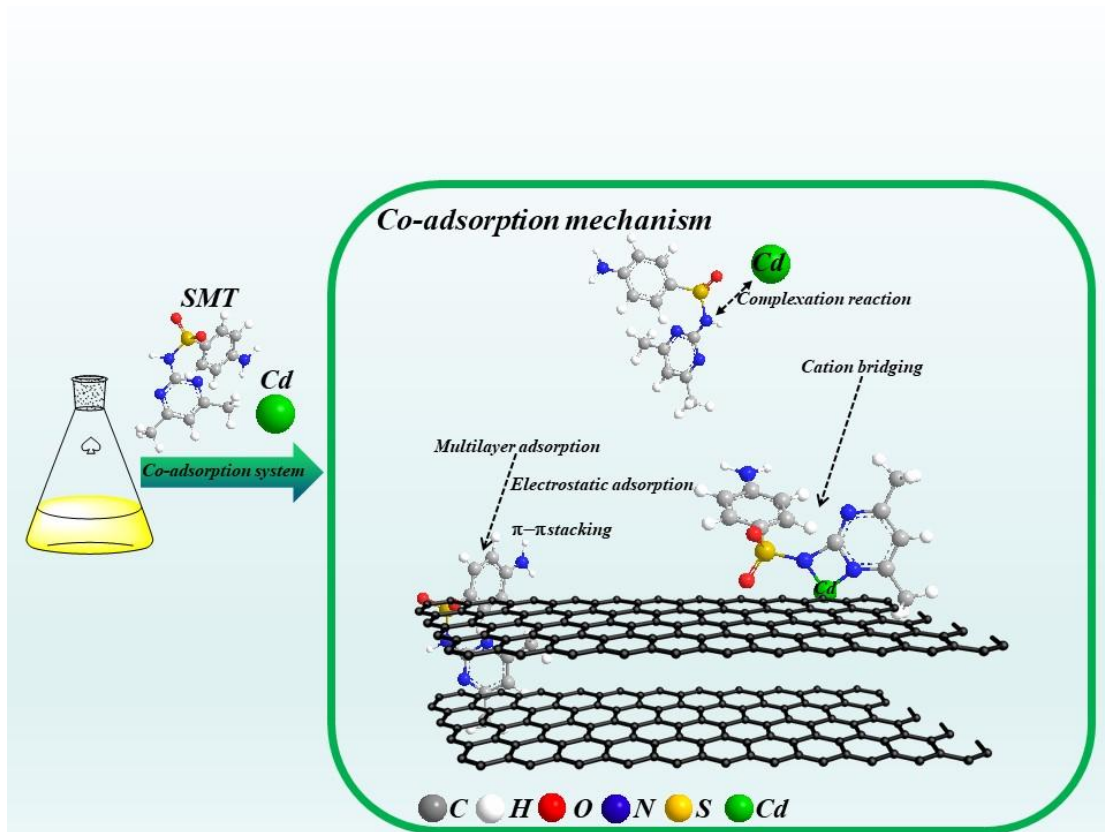
417 After cadmium ions are added to the system, they can form complexes with the SMT molecules and

418 the functional groups on the AC surface. Upon formation of a ternary SMT-Cd²⁺-AC complex, Cd²⁺

419 promotes the adsorption of SMT on activated carbon, acting as a bridge (as shown by XPS) indirectly

420 connecting SMT with the adsorbent[58]. The bridging effect of cadmium ions improves and promotes the

421 adsorption of SMT. As the adsorption of cadmium ions on activated carbon occurs in monolayer mode, when
422 their concentration is increased above the monolayer (reaching the adsorption equilibrium), the Cd ions
423 cannot further promote the adsorption of SMT, whose improvement is thus limited[25].
424



425
426 **Fig. 10.** Illustration of co-adsorption mechanism.

427

428 **4. Conclusion**

429

430 In this study, batch adsorption experiments were carried out in a single-pollutant (SMT/Cd²⁺) system
431 under different adsorbent dosage, contact time, and temperature conditions. The experimental results show
432 that the adsorption equilibrium of SMT is reached in approximately 12 h, and the pH value of the solution
433 affects the adsorption capacity of activated carbon. The adsorption by AC in alkaline conditions (pH = 9) is

434 weaker than that in acid conditions. The adsorption capacity of SMT decreases with increasing adsorbent
435 dosage, while the removal rate increases.

436 In the SMT-Cd²⁺ co-adsorption system, as the cadmium ion concentration is increased, the synergistic
437 effect of Cd²⁺ on the transport of SMT on activated carbon promotes its adsorption. The SMT adsorption
438 data conform to the Freundlich isotherm model, indicating the multilayer heterogeneous adsorption behavior
439 of SMT on AC. On the other hand, the adsorption of cadmium on AC can be described by the Langmuir
440 isotherm model, which suggests monolayer adsorption; therefore, no further promotion of SMT adsorption
441 can be achieved when the concentration of cadmium ions is increased above the monolayer coverage.

442 The characterization analysis showed the formation of a ternary AC-Cd²⁺-SMT complex at a certain
443 concentration of Cd²⁺. Cadmium act as a bridge indirectly connecting SMT with activated carbon, providing
444 further adsorption sites for SMT molecules in water. At the same time, the presence of cadmium ions
445 effectively reduces the electrostatic repulsion between SMT and activated carbon, thus promoting the
446 adsorption of SMT. Moreover, under neutral conditions, the complexation of Cd²⁺ with SMT shows a strong
447 correlation with the SMT adsorption amount ($R^2 = 0.84164$). Overall, the present results show that the
448 formation of a Cd²⁺-SMT complex has a significant effect on the adsorption of SMT. The current study also
449 emphasizes that, for a better understanding of the ecological risks associated with a pollutant, any
450 assessment of its environmental behavior should take into account the presence of other pollutants.

451

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